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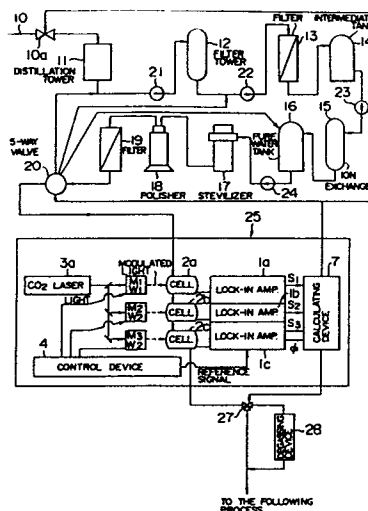
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**Method for analyzing impurities in liquid and apparatus therefor.**

A method for analyzing impurities in liquid and an apparatus therefor are disclosed, which are adapted to classify impurities contained in various liquids to be measured into soluble substance, insoluble substance and impurities in the form of bubbles and to measure their concentration separately; especially the impurities in liquid are analyzed by the method such that photoacoustic signals obtained by irradiating a liquid to be measured with intensity-modulated light are measured; the correlation between the modulation frequency of the intensity-modulated light (light modulation frequency) and the phase of the intensity-modulated light, with which the liquid to be measured is irradiated, as well as that of their photoacoustic signals are obtained; and impurities in the liquid to be measured are detected, while classifying them into soluble and insoluble ones and those in the form of bubbles on the basis of the information thus obtained: and the apparatus comprises a light source (3), at least one light modulator (5, M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub>) for transforming light from the light source (3) into intensity-modulated light having a given constant frequency, at least one cell (2, 2a, 2b, 2c) disposed at a position, where it is irradiated with the intensity-modulated light, and containing liquid to be measured, at least one phase detection device (1, 1a, 1b, 1c) for detecting the phase of the photoacoustic signals coming from the cell (2, 2a, 2b, 2c), a calculating device (7) for analyzing impurities in the liquid on the basis of this phase detection device

(1, 1a, 1b, 1c), and a control device (4) for controlling the modulation frequency (light modulation frequency) of the intensity-modulated light in the light modulator (5, M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub>).



METHOD FOR ANALYZING IMPURITIES IN LIQUID  
AND APPARATUS THEREFOR

1 BACKGROUND OF THE INVENTION

This invention relates to a method and an apparatus for analyzing impurities in liquid, and more particularly to a method and an apparatus for analyzing  
5 impurities in various kinds of liquid such as ultra-pure water adapted to classify the impurities into soluble substance, insoluble substance and impurities in the form of bubbles, and to measure their concentrations separately.

10 It is known that the photoacoustic spectroscopy is useful for a highly sensitive spectroscopic analyzing method, when it is applied to liquid samples and used as a colorimetric analyzing apparatus. Shohei Oda, Tsuguo Sawada and Hitoshi Kamada have reported in  
15 an article entitled "Determination of Ultra Trace Cadmium by Laser-Induced Photoacoustic Absorption Spectrometry", Analytical Chemistry, Vol. 52, p. 650 (1980), that cadmium can be analyzed down to 12 ppt in the form of a complex salt with dithizone by means of a  
20 photoacoustic analyzing apparatus. Further, Shohei Oda, Tsuguo Sawada, Toyohiko Moriguchi and Hitoshi Kamada have reported that when the photoacoustic analyzing method is applied to suspension of barium sulfate its detection limit is 30 ppb in an article entitled "Analysis of Turbid  
25 Solution by Laser-Induced Photoacoustic Spectroscopy",

1 Analytical Chemistry, Vol. 52, p. 650 (1980). It has  
been shown in this example that the calibration curve  
of the suspension doesn't depend on the diameter of  
particles, when light modulation frequency is set at  
5 33 Hz. That is, it has been clarified that the photo-  
acoustic analyzing method has a characteristic that it  
is not influenced by the diameter of suspended particles.

However, on the other hand, it has been  
varified by Kitamori, et al. that the phase of photo-  
10 acoustic signal depends on the diameter of suspended  
particles and that the diameter and the concentration of  
suspended particles can be measured by the photoacoustic  
analyzing method.

In this way, it has been verified that the  
15 photoacoustic analyzing method can be applied to highly  
sensitive analyzing and is useful not only for analysis  
of true solutions but also for that of suspensions.  
However, no technique has been known, which is adapted  
to measure separately not only insoluble impurities but  
20 also soluble ones (impurities in the form of ions) in  
liquid, utilizing such characteristics as described  
above of the photoacoustic analyzing method. This is  
because theoretical relations between measurement  
conditions such as the light modulation frequency for  
25 the photoacoustic analyzing apparatus and information  
obtained under those conditions are not known.

Furthermore, the amount of impurities contained  
in ultra-pure water is in the order of ppt's and this

1 concentration level is below the lower detection limit  
of the conventional analyzing method such as chromato-  
graphy, colorimetry, etc. Consequently, it is difficult  
to apply the prior art analyzing methods to analysis of  
5 impurities in ultra-pure water.

As stated above, none of the conventional  
impurity analyzing methods is adapted to analyze any  
kind of impurities such as fine particles whose concen-  
tration is very low (insoluble substance), substance in  
10 the form of ions (soluble substance), and further  
impurities in the form of bubbles. Furthermore there  
exists no apparatus for analyzing impurities in liquid  
permitting not only these analyses but also on-line  
measurements.

15 SUMMARY OF THE INVENTION

The object of this invention is to provide a  
method for analyzing impurities in liquid and an apparatus  
therefor, which are adapted to classify impurities in  
liquid to be measured into soluble and insoluble impurities  
20 as well as those in the form of bubbles, and to measure  
their concentration separately.

In one aspect of this invention, a method for  
analyzing impurities in liquid is carried out by measur-  
ing a photoacoustic signal obtained by irradiating onto  
25 a liquid to be measured an intensity-modulated light,  
obtaining the relationship between the modulation frequency  
of the intensity-modulated light (light modulation

1 frequency) and the phase of the photoacoustic signal,  
and determining the kinds of impurities in the liquid,  
as classified into soluble and insoluble ones and those  
in the form of bubbles on the basis of the information  
5 thus obtained.

In another aspect of this invention, there is  
provided an apparatus for analyzing impurities in liquid  
comprising a light source; at least one light modulator  
for transforming light from the light source into  
10 intensity-modulated light having a given constant  
frequency; at least one cell disposed at a position  
where it is irradiated with the intensity-modulated  
light and containing therein liquid to be measured; at  
least one phase detection device for detecting the phase  
15 of the photoacoustic signals coming from the cell; a  
calculating device for analyzing impurities in the  
liquid on the basis of information obtained by the phase  
detection device; and a control device for controlling  
the modulation frequency (light modulation frequency)  
20 of the intensity-modulated light derived from the light  
modulator.

According to this invention, a photoacoustic  
signal obtained by irradiating onto a liquid sample  
such as ultra-pure water an intensity-modulated light is  
25 measured and the kinds of impurities in the liquid sample  
as classified into soluble and insoluble substances and  
substance in the form of bubbles and the concentrations  
thereof are determined on the basis of the relation

1 between the modulation frequency (light modulation frequency) of the intensity-modulated light and the phase, as well as the intensity, of the photoacoustic signal.

Next, explanation will be made of the construction of the apparatus for measuring the kinds of impurities in liquid as classified into soluble and insoluble ones and those in the form of bubbles and the concentrations thereof on the basis of the relationship between the phase and the intensity of the photoacoustic  
5 signal and the light modulation frequency or the relationship between the phase set by the phase detection device for the photoacoustic signal and the light modulation  
10 frequency referring to Fig. 1 and Table 1.

Table 1 Measurement conditions and information

Light modulation frequency $\omega$	Phase of lock-in amp. $\theta$	Information source	Information
$\omega \ll \frac{3h}{\rho_s C_{ps} d_c}$	$\theta = \phi_Q$	S	Total amount of impurities
$\omega \gtrsim \frac{3h}{\rho_s C_{ps} d_c}$	$\theta = \phi_Q + \phi_D$	S $\phi_D$	Amount of insoluble impurities Center value of particle diameters
	$\theta = \phi_Q$	S	Amount of soluble impurities
	$\theta = 0$	S	Mixing of bubbles

1 Explanation of notation

$\rho_s$  : specific weight of particles

$C_{ps}$  : specific heat of particles

$h$  : heat transfer coefficient from particles to medium

$d_c$  : lower detection limit of radius of particles

$\phi_Q$  : phase delay due to propagation of photoacoustic signals

$\phi_D$  : phase delay due to delay in time necessary for heat evacuation after incidence of light to particles

$S$  : intensity of photoacoustic signals

The principle of this invention is based on the fact that the relation between the light modulation frequency and the phase of the photoacoustic signals varies depending on the property of impurities, as indicated in Table 1.

Hereinbelow, the principle on the basis of which the relation between the measurement conditions and information, as indicated in Table 1, can be obtained will be explained, according to the theory of the inventors of this invention on generation, propagation and detection of photoacoustic signals. Impurities absorbing periodically intensity-modulated light produce periodically heat by nonradiative processes. This heat induces periodical thermal expansion of the medium and as the result generates acoustic waves. The generated

1 acoustic waves, i.e. photoacoustic signals are represented  
 by  $P(\mathbf{r}, t)$ , where  $\mathbf{r}$  represents a vector in an  
 arbitrarily set spatial coordinate system and  $t$  represents  
 time. The photoacoustic signals can be described as  
 5 acoustic waves by the following wave equation;

$$(\nabla_{\mathbf{r}}^2 - \frac{1}{C^2} \frac{\partial}{\partial t}) P(\mathbf{r}, t) = - \frac{\beta}{C_P} \frac{\partial}{\partial t} H(\mathbf{r}, t)$$

..... (1), .

where  $C$  is the sound velocity,  $\beta$  is the thermal expansion  
 coefficient of the medium,  $C_P$  is the specific heat of the  
 medium,  $H(\mathbf{r}, t)$  represents the time and spatial  
 distribution of heat generated by the nonradiative  
 10 processes, and  $\nabla_{\mathbf{r}}$  is a differential operator with  
 respect to the vector  $\mathbf{r}$ . The solution of this wave is  
 in general given by the following equation;

$$P(\mathbf{r}, t) = F^{-1} \left[ - \frac{\beta}{C_P} \int_{\mathbf{r}'} \tilde{H}(\mathbf{r}', \omega) G(\mathbf{r} | \mathbf{r}') d_{\mathbf{r}'} \right]$$

..... (2)

where  $F$  is a Fourier transformation operator;  $\tilde{H}(\mathbf{r}', \omega)$ ,  
 etc. are Fourier images of a function  $H(\mathbf{r}, t)$ ; and  
 15  $G(\mathbf{r} | \mathbf{r}')$  is a Green function determined by the boundary  
 conditions given by the structure, materials, etc. of the  
 cell. The concrete representation of the photoacoustic  
 signals  $P(\mathbf{r}, t)$  is given by the structure and the

1 materials of the cell as well as the concrete representa-  
tion of the function  $H(r, t)$ .

In the case where the impurities are soluble,  
since the solution is a true solution, the spatial  
5 distribution of  $H(r, t)$  coincides with the spatial  
distribution of the projected light. Further, in the  
case where the nonradiative relaxation time of the  
impurities is sufficiently short and negligible with  
respect to the period of the light modulation, the  
10 time distribution of  $H(r, t)$  coincides with the time  
distribution of the projected light. Consequently, the  
following equation can be obtained;

$$H(r, t) = \alpha I_0 P_u(r) M(t) \dots\dots (3),$$

where  $\alpha$  is an absorption coefficient of the solution;  
 $I_0$  is the intensity of the projected light;  $R(r)$   
15 represents the spatial distribution of the projected  
light; and  $M(t)$  represents the time distribution of the  
projected light and is called the modulation function.  
Using Eqs. (2) and (3),  $P_1(r, t)$  representing the photo-  
acoustic signals for soluble impurities is given by a  
20 representation (4) as follows;

$$\begin{aligned} P_1(r, t) &= F^{-1} \left[ \frac{\alpha\beta}{C_P} I_0 i\omega \tilde{M}(\omega) \int_{r'} R(r') G(r|r') dr' \right] \\ &= \frac{\alpha\beta}{C_P} I_0 F^{-1} \left[ i\omega \tilde{M}(\omega) \int_{r'} R(r') G(r|r') dr' \right] \end{aligned} \dots\dots (4)$$

1           Next, in the case where the impurities are  
insoluble, a representation for the photoacoustic  
signals can be deduced as follows. As indicated in Fig.  
2, an impurity particle 41 absorbs light 42 and releases  
5 heat produced by a radiationless transition in the form  
of a thermal flux 43 in the medium. Representing this  
thermal flux by J, J is given by the following equation,  
which is produced according to a temperature field T(ρ, t)  
formed around the impurity particle;

$$J = -\lambda \vec{n} \cdot \nabla_{\rho} T(\rho, t) \quad \dots\dots (5),$$

10 where ρ indicates a vector representing the position of  
the impurity particle in the coordinate system; λ is  
the heat conduction coefficient of the medium; and  $\vec{n}$   
indicates the normal vector. The temperature field  
T(ρ, t) can be obtained by using the following heat  
15 equations;

$$\left(\nabla_{\rho}^2 - \frac{1}{K_S^2} \frac{\partial}{\partial t}\right) T(\rho, t) = -\frac{\alpha_S}{\lambda_S} R(r) M(t) \quad \dots\dots (6)$$

(ρ ∈ V)

$$\left(\nabla_{\rho}^2 - \frac{1}{K^2} \frac{\partial}{\partial t}\right) T(\rho, t) = 0 \quad \dots\dots (7)$$

(ρ ∉ V)

where K is the heat diffusion coefficient; W indicates  
the region inside of the impurity particle; and the

1 characters with suffix S indicate that the properties  
 represented by the respective characters are concerned  
 with the impurity particle. In the case where impurity  
 particles are distributed uniformly in the cell, H(r, t)  
 5 can be obtained by using the following equation;

$$H(\mathbf{r}, t) = H \int_S - \lambda \vec{n} \cdot \nabla_{\rho} T(\rho, t) d\rho \quad \dots\dots (8),$$

where N is the density in number of the impurity particles  
 and it is related to the impurity concentration C by the  
 following equation;

$$C = \frac{N}{V \sigma_S} \quad \dots\dots (9),$$

where  $\sigma$  indicates the density and V represents the volume  
 10 of the impurity particles.  $\int_S$  in Eq. (8) indicates  
 integration over the surfaces of the impurity particles.  
 In the case where the impurity particles are sufficiently  
 small and the temperature of all the impurity particles  
 varies uniformly, by resolving Eqs. (5) to (9),  $\tilde{H}(\mathbf{r}, \omega)$   
 15 is represented by Eq. (10) as follows;

$$\tilde{H}(\mathbf{r}, \omega) = -\frac{\lambda}{\lambda_S} \frac{C}{\sigma_S} \alpha_S I_0 R(\mathbf{r}) \tilde{M}(\omega) \times \frac{\frac{S}{V} h}{\sigma_S C_{PS} i\omega + \frac{S}{V} h} \quad \dots\dots (10).$$

Substituting  $\tilde{H}(\mathbf{r}, \omega)$  of Eq. (10) for Eq. (2),

1 the photoacoustic signals  $P_2(r, t)$  coming from the impurity particles can be obtained by using the following equation;

$$P_2(r, t) = \frac{\beta}{C_P} \frac{\lambda}{\lambda_S} \frac{C}{\sigma_S} \alpha_S I_0 F^{-1} [\tilde{D}(\omega) \tilde{M}(\omega) \times i\omega \int_{r'} R(r') G(r|r') dr'] \dots\dots (11),$$

where

$$\tilde{D}(\omega) = \frac{\frac{S}{V} h}{\sigma_S C_{PS} i\omega + \frac{S}{V} h} \dots\dots (12).$$

When the modulation function  $M(t)$  is a sinusoidal function having an angular frequency  $\omega_0$ , since

$$\tilde{M}(\omega) = \delta(\omega - \omega_0) \dots\dots (13),$$

Eqs. (4) and (11) can be transformed into the following equations;

$$P_1(r, t) = \frac{\beta}{C_P} \alpha I_0 Q(r, t) e^{i\omega_0 t} \dots\dots (14),$$

$$P_2(r, t) = -\frac{\beta}{C_P} \frac{\lambda}{\lambda_S} \frac{C}{\sigma_S} \alpha_S I_0 \tilde{D}(\omega_0) Q(r, t) \cdot e^{i\omega_0 t} \dots\dots (15),$$

where

$$Q(r, t) = i\omega_0 \int_{r'} R(r') G(r|r') dr' \dots\dots (16).$$

1 When the diameter of impurity particles is nearly zero,  
 Eq. (15) coincides with Eq. (14) and the photoacoustic  
 signals from a liquid containing insoluble impurities  
 become identical to those from a true solution. In  
 5 order to make the intensity and the phase of the photo-  
 acoustic signals more distinctive, Eqs. (14) and (15)  
 may be represented in a polar coordinate system, as  
 follows;

$$P_1(r, t) = \frac{\beta}{C_P} \alpha I_0 Q e^{i(\omega_0 t - \phi_Q)} \quad \dots\dots (17)$$

$$P_2(r, t) = \frac{\beta}{C_P} \frac{\lambda}{\lambda_S} \frac{C}{\sigma_S} \alpha_S I_0 \tilde{D} Q e^{i(\omega_0 t - \phi_D - \phi_Q)} \quad \dots\dots (18),$$

where

$$Q = |Q(r, t)| \quad \dots\dots (19)$$

$$\tilde{D} = |\tilde{D}(r, t)| \quad \dots\dots (20)$$

$$\phi_Q = \tan^{-1} \frac{I_m Q(r, A)}{R_e Q(r, t)} \quad \dots\dots (21)$$

$$\phi_D = \tan^{-1} \frac{\sigma_S C_{PS} V}{hS} \omega_0 \quad \dots\dots (22).$$

Consequently,  $\phi_Q$  represents the phase delay due to  
 10 propagation of the photoacoustic signals and  $\phi_D$  indicates  
 the phase delay of the photoacoustic signal due to the

1 time interval required for release of heat produced in  
the impurity particles.

By using Eqs. (12) to (22), the conditions  
for the classification of the impurities and the measure-  
5 ment of their concentrations, as indicated in Table 1,  
can be obtained. At first, in the case where the light  
modulation angular frequency  $\omega_0$  sufficiently satisfies

$$\sigma_S C_{PS} \omega_0 \ll \frac{S}{V} h \quad \dots \quad (23),$$

and the following equation is valid;

$$\tilde{D}(\omega_0) = 1,$$

it can be seen from Eq. (18) that the intensity of the  
10 photoacoustic signal is independent of the size of the  
impurity particles. Furthermore, in this case, from  
Eq. (22)

$$\phi_D = 0$$

can be obtained. Thus, only  $\phi_Q$  gives the phase delay  
of the photoacoustic signal in Eqs. (17) and (18) so  
15 that the phase of the photoacoustic signal from the  
liquid containing insoluble impurities coincides with  
that from a solution containing soluble impurities.  
Since the photoacoustic signal is an acoustic wave having  
linear characteristics, the principle of superposition

1 is applied to the signal. Under these conditions, the  
intensity of the photoacoustic signal corresponds to  
the sum of the concentration of soluble impurities and  
that of insoluble ones and the resultant phase is  $\phi_Q$ .  
5 Therefore, when the phase  $\theta$  of the lock-in amplifier for  
the photoacoustic signal is set at

$$\theta = \phi_Q ,$$

the intensity of the phase-detected photoacoustic signal  
represents the total amount of impurities contained in  
the solution. On the other hand, when  $\omega_0$  satisfies

$$\sigma_S C_{Ps} \omega_0 \gtrsim \frac{S}{V} h \quad \dots\dots (24)$$

10 and  $\phi_D$  is distinguishable from  $\phi_Q$ , it can be understood  
that the insoluble impurities can be measured separately  
from soluble ones. In this case, the size of the  
impurity particles can be known from Eq. (22) and thus,  
in the case where the impurities particles can be  
15 assumed to be spherical, since  $S = 4\pi d^2$  and  $V = \frac{4}{3}\pi d^3$  in  
Eq. (22), the radius  $d$  of the impurity particles is  
given by

$$d = \frac{3h \tan \phi_D}{\sigma_S C_{Ps} \omega_0} \quad \dots\dots (25)$$

In addition, for the conditions given by Eqs. (23) and

1 (24) the following relationship is valid;

$$\frac{S}{V} h = \frac{3h}{d} \dots\dots (26).$$

This means that, in the case where  $\phi_D = 0$ , even if the projected light is modulated with a light modulation frequency satisfying Eq. (24), the impurities are not  
5 particles but all of them are soluble.

In the case where the impurities are in the form of bubbles, the projected light is refracted by bubbles, changes its path and can enter directly the detector. In this case, the incident light produces  
10 photoacoustic signals of the detector itself. However, since the light velocity is much greater than the sound velocity, the phase of the photoacoustic signal is zero. Consequently, it is possible to measure bubbles, distinguishing them from soluble and insoluble impuri-  
15 ties.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a block diagram showing the basic structure of this invention;

Fig. 2 is a schematic diagram for explaining  
20 the process of absorbing light and releasing heat;

Fig. 3 is a block diagram showing the first embodiment of this invention;

Fig. 4 is a system diagram showing the second embodiment of this invention;

1            Fig. 5 shows graphs indicating measurement  
examples obtained by using the apparatus indicated in  
Fig. 4;

            Fig. 6 is a system diagram showing the third  
5 embodiment of this invention;

            Fig. 7 is a system diagram showing the fourth  
embodiment of this invention; and

            Fig. 8 shows graphs indicating measurement  
examples obtained by using the apparatus indicated in  
10 Fig. 7.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

            Hereinbelow the embodiments of this invention  
will be explained, referring to the drawing.

            Fig. 1 is a block diagram showing the basic  
15 structure of this invention. Light emitted by a light  
source enters a light modulator 5, in which the incident  
light is transformed into intensity-modulated light,  
whose intensity varies with a constant frequency, and  
a cell 2 containing a liquid sample to be measured is  
20 irradiated with this intensity-modulated light. The  
reference numeral 1 represents a phase detection device  
having functions to receive photoacoustic signals  
obtained at the cell 2 and measure the phase and the  
intensity of the photoacoustic signal or to take out  
25 only the photoacoustic signal which has a given phase  
from the received signal and measure its intensity.  
The reference numeral 4 indicates a control device, which

1 sets the light modulation frequency in the light modulator  
5 and also the phase in the phase detection device 1.  
The reference numeral 7 represents a calculating device,  
which classifies impurities contained in the liquid  
5 sample, calculates their amount (concentration), and  
displays results, if necessary, on the basis of infor-  
mation obtained by the phase detection device 1.

Fig. 3 shows the first embodiment of an appara-  
tus for analyzing impurities in liquid, in which the  
10 light modulation frequency can be set at any desired  
value and a lock-in amplifier is used as the phase  
detection device 1 for detecting the phase of the  
photoacoustic signals, the phase and the sensitivity of  
the lock-in amplifier 1 also being settable at any  
15 desired values. The light modulation frequency as  
well as the phase and the sensitivity of the lock-in  
amplifier are controlled by the control device coupled  
with a calculator on the basis of Table 1. In this  
embodiment a sample such as ultra-pure water, etc. is  
20 prepared and filled in a sealed type cell 2 and the  
photoacoustic signal derived from the sample is measured.  
In this apparatus an Ar laser device is used as the  
light source 3 and a light beam of 2.6 W having an  
oscillation line of 488 nm is utilized as exciting  
25 light. In this apparatus, the light modulation frequency  
is set at 80 Hz for low frequency modulation and at 410  
kHz for high frequency modulation. These light modula-  
tion frequencies sufficiently satisfy Eqs. (23) and (24),

1 respectively, for particles of silicon dioxide having a  
radius of 1  $\mu\text{m}$  in water. Once the low frequency modula-  
tion is selected, the phase of the lock-in amplifier 1  
is set automatically at a value as mentioned before by  
5 the controller (control device) 4 and measures only the  
intensity of the photoacoustic signal. In this way, the  
total amount of impurities (concentration) in the sample  
can be obtained. In this case, the lower detection  
limit of the light-absorption coefficient is about  
10  $10^{-8}/\text{cm}$ . Further, when the impurities are silicon  
dioxide particles, they can be measured down to about  
20 ppt. When the measurement of the total amount of  
impurities is terminated, the light modulation frequency  
is set automatically at the high frequency side and  
15 the lock-in amplifier acts as a phase detector. In this  
case, for a particle radius of 1  $\mu\text{m}$  the phase is 45  
degrees and the smallest measurable value of the phase  
detector of 0.5 degree corresponds to a particle radius  
of about 0.1  $\mu\text{m}$ .

20 In addition, in the embodiment shown in Fig.  
3, the reference numeral 5 is the photoacoustic modulator  
transforming light coming from the Ar laser 3 into  
modulated light; 6 is the oscillator feeding the lock-in  
amplifier 1 and the photoacoustic modulator 5 with  
25 signals; and 7 represents the calculator (calculating  
device). Further, since a photoacoustic modulator 5 is  
used as the light modulator 5, an oscillator 6 is disposed,  
which drives the modulator.

1           Next, the second embodiment of the apparatus  
according to this invention will be explained, referring  
to Fig. 4. In this embodiment, flow type cells are used  
and 2 sets of light modulators  $M_1$ ,  $M_2$ , cells 2a, 2b  
5 combining the same sample and lock-in amplifiers 1a, 1b  
are disposed. These 2 sets are adjusted for different  
measurement conditions. The light source 3 is an Ar  
laser device having an output 20 W. The light modulator  
 $M_1$  is set at 80 Hz and  $M_2$  at 410 kHz. The setting  
10 value of these light modulation frequencies can be varied  
by the control device 4. The lock-in amplifier 1a  
measures the intensity  $S_1$  and 1b measures variations in  
phase  $\phi_D$  and the intensity  $S_2$ . The measured values  $S_1$ ,  
 $S_2$  and  $\phi_D$  are processed by a calculator 7. Further,  
15 in the figure, the reference numeral 8 indicates a  
light distributing device disposed between the light  
source 3 and the light modulators  $M_1$ ,  $M_2$ , that is, 8a  
is a beam splitter, which directs the incident light  
beam toward 2 directions, and 8b is a mirror, which  
20 reflects the incident beam. The liquid sample 35 flows  
successively through the cells 2a and 2b by means of a  
pump 36. Fig. 5 shows an example of measurements accord-  
ing to this embodiment. The figure shows that soluble  
impurities of 20 ppb flows in the region A and impurities  
25 of 60 ppt having a particle radius of 0.3  $\mu\text{m}$  are detected  
in the region B. In the region C impurities of 30 ppt  
in the form of particles having a particle radius of  
0.15  $\mu\text{m}$  are detected. In the region D no impurities are

1 detected. The relationship between the intensity of  
signals and the concentration in this apparatus is as  
follows;

Soluble impurity concentration

$$= \text{signal intensity } (\mu\text{V}) \times 2 \text{ (ppb}/\mu\text{V}) \dots (27)$$

Insoluble impurity concentration

$$= \text{signal intensity } (\mu\text{V}) \times 2 \text{ (ppt}/\mu\text{V}) \dots (28)$$

In this case, for the soluble impurities,  
5 calculations were effected, assuming that the molecular  
light absorption coefficient is  $10 \text{ (mol. cm}^{-2}\text{)}$ .

Furthermore, it can be seen that at E and F  
bubbles are detected.

Fig. 6 shows the third embodiment of this  
10 invention, in which the method according to this invention  
is applied to an ultra-pure water production apparatus.

In the figure, the reference numeral 10 indicates  
a raw water supply line for feeding a distillation tower  
11 with raw water such as city water; 12 is an activated  
15 charcoal filter tower for eliminating organic impurities;  
13 is an inverse osmotic membrane module for eliminating  
particles, electrolyte, etc.; 14 is an intermediate tank;  
15 is an ion exchange resin tower for eliminating  
electrolyte, etc.; 16 is a pure water tank for storing  
20 produced pure water (specific resistance greater than  
 $1 - 10 \text{ M}\Omega\text{cm}$ ); 17 is an ultra-violet ray sterilizer for  
sterilizing bacteria; 18 is a polisher for eliminating  
electrolyte; and 19 is an ultra-filtration membrane  
module for eliminating fine particles. This ultra-

1 filtration membrane module 19 feeds a 5-way valve 20  
with ultra-pure water, whose specific resistance is  
greater than 17-18 M $\Omega$ cm and in which the number of fine  
particles larger than 0.1-0.2  $\mu$ m is smaller than 50/cc  
5 and that of living bacteria is smaller than 0.1/cc.  
Further, in the figure, 21 to 24 represent water sending  
pumps or pressuring pumps.

Produced ultra-pure water is supplied  
successively from the 5-way valve 20 to the cells 2a,  
10 2b and 2c of the apparatus 25 for analyzing impurities.  
3a indicates a light source utilizing a high energy CO<sub>2</sub>  
laser; 9a is a beam splitter; 9c is a half mirror;  
9b is a mirror; M<sub>1</sub>, M<sub>2</sub> and M<sub>3</sub> are light modulators; 1a,  
1b and 1c are lock-in amplifiers; 4 is a controlling  
15 device controlling the light modulators M<sub>1</sub> to M<sub>3</sub> and the  
lock-in amplifiers 1a to 1c; and 7 is a calculating  
device for classifying impurities into various sorts  
and calculating their concentration on the basis of  
information coming from the lock-in amplifiers 1a to 1b.  
20 This calculating device 7 is provided also with the  
function to control a valve 10a mounted on the raw water  
supply line 10, the 5-way valve 20 and another valve  
27, depending on analysis results of the produced ultra-  
pure water. The light modulation frequency  $\omega_1$  of the  
25 light modulator M<sub>1</sub> is set at 33 Hz and the light  
frequencies  $\omega_2$  and  $\omega_3$  of the light modulators M<sub>2</sub> and M<sub>3</sub>,  
respectively, are set at 4 MHz. The phase of the lock-in  
amplifiers 1a and 1b is set at  $\phi_D = 48^\circ$  obtained

1 previously experimentally. The total amount of impurities  
and the amount of soluble impurities are measured on  
the basis of the intensity of the photoacoustic signals  
 $S_1$  and  $S_2$ , respectively. The lock-in amplifier 1c  
5 measures the phase  $\phi$  and the intensity  $S_3$  of the photo-  
acoustic signals. Thus, the mean radius of particles  
of insoluble impurities is obtained from the phase  $\phi$  and  
the concentration of the insoluble impurities is calculated  
on the basis of the intensity  $S_3$ . The signals coming from  
10 the lock-in amplifiers 1a-1c are directly inputted to  
the calculating device 26 and control the 5-way valve  
20 described above as follows.

- If  $S_1 > 100 \mu V \rightarrow$  Stop of water supply  
(the valve 10a is closed.)
- 15 • If  $S_2 > 50 \mu V \rightarrow$  Redoing of purification after the  
inverse osmotic membrane module 13 or the ion  
exchange resin tower 15.
- If  $S_3 > 50 \mu V$  and at the same time  $\phi > 0.5^\circ \rightarrow$  Redoing  
of purification by returning water to the upstream  
20 of the pure water tank 16 or the ultra-filtration  
membrane module.

For the above described conditions it is assumed  
that purification is repeated, if the amount of soluble  
impurities is greater than about 1 ppb and if the amount  
25 of insoluble impurities is greater than 10 ppt and at  
the same time their particle radius is greater than 0.3  
 $\mu m$ . Further, when the phase of the lock-in amplifier 1c

1 is 0, since bubbles are mixed in the ultra-pure water,  
the valve 27 is commuted to the side of a degassing  
device 28 and after having degassed the ultra-pure water,  
it is supplied to a use point for example for semi-  
5 conductor production.

Furthermore, although all the produced ultra-  
pure water passes through the apparatus for analyzing  
impurities 25 in this embodiment, in the case where the  
capacity of the pure water production apparatus is large,  
10 the analyzing apparatus 25 can be also so constructed  
that only a part of the produced ultra-pure water is  
bypassed therethrough.

Fig. 7 shows the fourth embodiment of this  
invention, in which an apparatus for analyzing impurities  
15 according to this invention is applied to industrial  
waste water. In the figure, the reference numerals,  
which are used also in Fig. 4 or Fig. 6, represent  
identical or corresponding parts.

The reference numeral 29 indicates a waste  
20 water ejecting line; 30 is a waste water treatment  
installation; 31 is a storing reservoir; and 32 is a  
sampling device. Samples taken in this sampling device  
32 are supplied successively to the cells 2a, 2b and  
2c of the apparatus for analyzing impurities. In this  
25 embodiment an Ar laser device of 5 W is used as the  
light source 3. The other conditions are identical to  
those described for the embodiment illustrated in Fig.  
6. The photoacoustic signals (PA signals) coming from

1 the cells 2a to 2c are inputted to the lock-in amplifiers  
1a to 1c, respectively, and the intensities  $S_1$  to  $S_3$  of  
the photoacoustic signals from the lock-in amplifiers  
1a to 1c as well as the phase  $\phi_D$  of the photoacoustic  
5 signals from the lock-in amplifier 1c are inputted to  
the display-recording device (calculating device) 7.  
The samples, which have passed through the cells 2a to  
2c, are ejected by the drain.

Fig. 8 shows a result obtained by analyzing  
10 industrial waste water by means of the apparatus indicated  
in Fig. 7.

As indicated above, the apparatus for analyzing  
impurities according to this invention can be applied  
to the case where samples to be analyzed are turbid and  
15 suspended.

According to the embodiments described above  
of this invention the following effects can be obtained.

- 1) It is possible to classify impurities into  
soluble and insoluble ones as well as bubbles in liquid  
20 and to measure their concentration separately.
- 2) It is possible to analyze an extremely small  
amount of impurities (order of ppt), because the photo-  
acoustic spectroscopic method is applied to the detection.
- 3) It is possible to analyze also turbid samples,  
25 because the photoacoustic spectroscopic method is  
utilized for the detector.
- 4) It is possible to monitor impurities in liquid,  
because on-line measurement can be effected. Consequently,

1 when this method is applied to the water quality control  
of ultra-pure water, on-line control of the water quality  
can be effected and production yield in semiconductor  
process and genetic engineering plant is increased.

5           As explained above, according to this inven-  
tion, since impurities in liquid are analyzed on the  
basis of information on the modulation frequency of  
intensity-modulated light, with which liquid samples  
are irradiated, the relationship between the phase of  
10 the intensity-modulated light and that of the photo-  
acoustic signal, and the intensity of the photoacoustic  
signal, it is possible to classify impurities in liquid  
into soluble and insoluble ones and those in the form  
of bubbles and also to measure their concentration  
15 separately.

CLAIMS:

1. A method for analyzing impurities in liquid, in which photoacoustic signals obtained by irradiating a liquid to be measured with intensity-modulated light are measured; the relationship between the modulation frequency of said intensity-modulated light (light modulation frequency) and the phase of said intensity-modulated light, with which the liquid to be measured is irradiated, as well as that of said photoacoustic signals is obtained; and impurities in the liquid to be measured are detected, while classifying them into solubled and insoluble ones and those in the form of bubbles on the basis of the information thus obtained.

2. A method for analyzing impurities in liquid according to Claim 1, in which in the case where the total amount of impurities in liquid should be measured, the light modulation frequency  $\omega$  is determined so that it satisfies;

$$\omega_1 \ll \frac{3h}{\rho_S C_{pS} d_c} ,$$

where  $\rho_S$  is the specific weight of particles to be measured;  $C_{pS}$  is the specific heat of the particles;  $d_c$  is the lower detection limit of the radius of the particles; and  $h$  represents the heat transfer coefficient from the particles to the medium; the phase  $\theta$  of the phase detection device (1, 1a, 1b, 1c) for detecting the phase of the photoacoustic signals being set so that it

satisfies;

$$\theta = \phi_Q ,$$

where  $\phi_Q$  indicates the phase delay due to the propagation of the photoacoustic signals; and the total amount of impurities in liquid is calculated on the basis of the intensity of the photoacoustic signals thus phase-detected.

3. A method for analyzing impurities in liquid according to Claim 1, in which in the case where the total amount of impurities in liquid should be measured separately, the light modulation frequency  $\omega$  is determined so that it satisfies;

$$\omega \gg \frac{3h}{\rho S C_{Ps} dc} ,$$

where  $\rho S$  is the specific weight of particles to be measured;  $C_{Ps}$  is the specific heat of the particles;  $dc$  is the lower detection limit of the radius of the particles; and  $h$  represents the heat transfer coefficient from the particles to the medium; and the impurities are detected, while classifying them into soluble and insoluble ones and those in the form of bubbles on the basis of the phase of the photoacoustic signals thus obtained.

4. A method for analyzing impurities in liquid according to Claim 3, in which, when the phase  $\theta$  of the photoacoustic signals with respect to the phase of the

intensity-modulated light, with which the liquid to be measured is irradiated, satisfies;

$$\theta = 0 \quad ,$$

it is judged that bubbles are mixed therein; when

$$\theta = \phi_Q \quad ,$$

where  $\phi_Q$  indicates the phase delay due to the propagation of the photoacoustic signals, it is judged that soluble impurities are mixed therein; and further when

$$\theta = \phi_Q + \phi_D \quad ,$$

where  $\phi_D$  is the phase delay due to the time which elapses from irradiation of the particle with light to release of heat, it is judged that insoluble impurities are mixed therein.

5. A method for analyzing impurities in liquid according to Claim 4, in which impurities are classified into soluble and insoluble ones as well as those in the form of bubbles on the basis of the phase  $\theta$  of the photoacoustic signals thus detected and their concentration is obtained on the basis of the intensity of the photoacoustic signals.

6. A method for analyzing impurities in liquid according to Claim 5, in which, when the phase  $\theta$  of the

photoacoustic signals is represented by

$$\theta = \phi_Q + \phi_D ,$$

the mean particle radius of the insoluble impurities is calculated on the basis of the value of  $\phi_D$ .

7. A method for analyzing impurities in liquid according to Claim 1, in which the liquid to be measured is ultra-pure water.

8. An apparatus for analyzing impurities in liquid comprising:

a light source (3);

at least one light modulator (5,  $M_1$ ,  $M_2$ ,  $M_3$ )

transforming light from said light source (3) into intensity-modulated light having an arbitrary constant frequency;

at least one cell (2, 2a, 2b, 2c) disposed at a position, where it is irradiated with said intensity-modulated light and containing liquid to be measured;

at least one phase detection device (1, 1a, 1b, 1c) for detecting the phase of the photoacoustic signals coming from the cell (2, 2a, 2b, 2c);

a calculating device (7) for analyzing impurities in the liquid on the basis of information coming from this phase detection device (1, 1a, 1b, 1c); and

a control device (4) for controlling the modulation frequency (light modulation frequency) of the intensity-modulated light in said light modulator (5,  $M_1$ ,  $M_2$ ,  $M_3$ ).

9. An apparatus for analyzing impurities in liquid according to Claim 8, in which said phase detection device (1, 1a, 1b, 1c) has a function to detect photoacoustic signals having a predetermined phase among those received by it, and a control device is disposed for setting said predetermined phase.

10. An apparatus for analyzing impurities in liquid according to Claim 9, in which only one control device (4) controls said light modulator (5,  $M_1$ ,  $M_2$ ,  $M_3$ ) as well as said phase detection device (1, 1a, 1b, 1c).

11. An apparatus for analyzing impurities in liquid according to Claim 8 or 9, in which said phase detection device (1, 1a, 1b, 1c) has a function to amplify the photoacoustic signals thus obtained and the control device (4) of said phase detection device (1, 1a, 1b, 1c) controls its phase as well as its sensitivity.

12. An apparatus for analyzing impurities in liquid according to Claim 8, in which said calculating device (7) for analyzing impurities analyzes the kind and the amount of the impurities contained in the liquid on the basis of the phase and the intensities of the photoacoustic signals coming from said phase detection device (1, 1a, 1b, 1c).

13. An apparatus for analyzing impurities in liquid according to Claim 12, in which, when insoluble impurities are detected in the liquid to be measured, said calculating device (7) calculates the particle radius of impurities on the basis of the phase of the photoacoustic signals

thus detected.

14. An apparatus for analyzing impurities in liquid according to Claim 8, in which, in the case where the total amount of the impurities should be measured, said control device (4) controls said light modulator (5,  $M_1$ ,  $M_2$ ,  $M_3$ ) and said phase detection device (1, 1a, 1b, 1c) so that the light modulation frequency  $\omega$  of said light modulator (5,  $M_1$ ,  $M_2$ ,  $M_3$ ) satisfies;

$$\omega \ll \frac{3h}{\rho S C_{Ps} d_c} ,$$

where  $\rho S$  is the specific weight of particles to be measured;  $C_{Ps}$  is the specific heat of the particles;  $d_c$  is the lower detection limit of the radius of the particles; and  $h$  represents the heat transfer coefficient from the particles to the medium; and at the same time the phase  $\theta$  of the phase detection device (1, 1a, 1b, 1c) for detecting the phase of the photoacoustic signals satisfies;

$$\theta = \phi_Q ,$$

where  $\phi_Q$  indicates the phase delay due to the propagation of the photoacoustic signals.

15. An apparatus for analyzing impurities in liquid according to Claim 8 or 13, in which impurities in the liquid should be measured separately, while classifying them into soluble and insoluble ones as well as those in

the form of bubbles, said control device (4) controls said light modulator (5, M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub>) so that the light modulation frequency  $\omega$  of said light modulator (5, M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub>) satisfies;

$$\omega_1 \gtrsim \frac{3h}{\rho S C_{ps} dc} ,$$

where  $\rho S$  is the specific weight of particles to be measured;  $C_{ps}$  is the specific heat of the particles;  $dc$  is the lower detection limit of the radius of the particles; and  $h$  represents the heat transfer coefficient from the particles to the medium.

16. An apparatus for analyzing impurities in liquid according to Claim 15, in which said calculating device (7) calculates the kind and the amount of the impurities contained in the liquid on the basis of the phase and the intensity of the photoacoustic signals coming from said phase detection device (1, 1a, 1b, 1c) and at the same time, when insoluble impurities are detected therein, said calculating device (7) calculates also the particle radius of said insoluble impurities contained therein.

17. An apparatus for analyzing impurities in liquid according to Claim 16, in which a display device is disposed for displaying the kind and the amount of the impurities as well as the particle radius of the insoluble impurities.

18. An apparatus for analyzing impurities in liquid

according to Claim 11, in which said phase detection device (1, 1a, 1b, 1c) is a lock-in amplifier.

19. An apparatus for analyzing impurities in liquid according to Claim 18, in which said light modulator (5,  $M_1$ ,  $M_2$ ,  $M_3$ ) is a photoacoustic modulator and an oscillator (6) is disposed between said light modulator (5,  $M_1$ ,  $M_2$ ,  $M_3$ ) and said control device (4) for controlling them, whereby the light modulation frequency of said light modulator (5,  $M_1$ ,  $M_2$ ,  $M_3$ ) is controlled by controlling the oscillation frequency of said oscillator (6) by means of said control device (4) and reference signals coming from said oscillator (6) are given said lock-in amplifier.

20. An apparatus for analyzing impurities in liquid according to Claim 8, in which a plurality of sets, each of which consists of a light modulator (5,  $M_1$ ,  $M_2$ ,  $M_3$ ), a cell (2a, 2b, 2c), and a phase detection device (1, 1a, 1b, 1c), for analyzing photoacoustic signals are arranged in parallel to each other so that each of a plurality of light beams coming from said light source (3) enters the cell (2a, 2b, 2c) of each of the sets, the light modulation frequencies in different light modulators being so controlled that they are different from each other; at the same time the liquid to be measured flowing through the cells (2a, 2b, 2c) one after another.

21. An apparatus for analyzing impurities in liquid according to Claim 20, in which two light modulators ( $M_1$ ,  $M_2$ ), two cells (2a, 2b), and two phase detection

devices (1a, 1b) are disposed in parallel, respectively, so that the first and the second analyzing sets are constructed; for said first analyzing set the light modulation frequency  $\omega_1$  being so controlled that it satisfies;

$$\omega_1 \ll \frac{3h}{\rho S C_{Ps} dc} ,$$

where  $\rho S$  is the specific weight of particles to be measured;  $C_{Ps}$  is the specific heat of the particles;  $dc$  is the lower detection limit of the radius of the particles; and  $h$  represents the heat transfer coefficient from the particles to the medium; the phase  $\theta$  of the phase detection device (1a, 1b) for detecting the phase of the photoacoustic signals being set so that it satisfies;

$$\theta = \phi_Q ,$$

where  $\phi_Q$  indicates the phase delay due to the propagation of the photoacoustic signals; and further for said second analyzing set the light modulation frequency  $\omega_2$  is so controlled that it satisfies;

$$\omega_2 \gg \frac{3h}{\rho S C_{Ps} dc} .$$

22. An apparatus for analyzing impurities in liquid according to Claim 20 or 21, in which there exists only one light source (3) and a light distributing device

(8, 9a, 9b, 9c) is disposed between said light source (3) and each of said light modulators ( $M_1, M_2, M_3$ ) so that light emitted by said light source (3) is splitted into a plurality of light beams, each of which enters each of said light modulators ( $M_1, M_2, M_3$ ).

23. An apparatus for analyzing impurities in liquid according to Claim 22, in which said light distributing device (8) consists of a beam splitter (8a) and a mirror (8b).

24. An apparatus for analyzing impurities in liquid according to Claim 20, in which the number of analyzing sets is greater than two and said light distributing device consists of a beam splitter (9a), at least one half mirror (9c), and a mirror (9b).

25. An apparatus for analyzing impurities in liquid according to Claim 20, in which three light modulators ( $M_1, M_2, M_3$ ), three cells (2a, 2b, 2c) and three phase detection devices (1a, 1b, 1c) are disposed in parallel, respectively, so that the first, the second and third analyzing sets are constructed; for said first analyzing set the light modulation frequency  $\omega_1$  being so controlled that it satisfies;

$$\omega_1 \ll \frac{3h}{\rho S C_{Ps} dc} ,$$

where  $\rho S$  is the specific weight of particles to be measured;  $C_{Ps}$  is the specific heat of the particles;  $dc$  is the lower detection limit of the radius of the particles;

and  $h$  represents the heat transfer coefficient from the particles to the medium; for said second and third analyzing sets the light modulation frequency  $\omega_2$  being so controlled that it satisfies;

$$\omega_2 \approx \frac{3h}{\rho S C_{Ps} dc} ;$$

for the first and second analyzing sets the phase  $\theta$  of the phase detection device (1a, 1b) for detecting the phase of the photoacoustic signals being set so that it satisfies;

$$\theta = \phi_Q ,$$

where  $\phi_Q$  indicates the phase delay due to the propagation of the photoacoustic signals; whereby the concentration of the whole impurities is calculated on the basis of the intensity ( $S_1$ ) of the photoacoustic signals coming from the phase detection device (1a) of said first analyzing set; the concentration of the soluble impurities is calculated on the basis of the intensity ( $S_2$ ) of the photoacoustic signals coming from the phase detection device (2a) of said second analyzing set; and the concentration and the particle radius of the insoluble impurities are calculated or bubbles are detected on the basis of the intensity ( $S_3$ ) and the phase  $\theta$  of the photoacoustic signals coming from the phase detection device (3a) of said third analyzing set.

26. An apparatus for analyzing impurities in liquid according to Claim 25, in which the liquid to be analyzed is ultra-pure water produced by means of an ultra-pure water production apparatus (25) and the whole or a part bypassed of the ultra-pure water thus produced flows through the cells of said first to third analyzing sets one after another so that the impurities contained in the ultra-pure water are analyzed.

27. An apparatus for analyzing impurities in liquid according to Claim 26, in which a commuting valve (10a) is disposed between said ultra-pure water production apparatus and an ultra-pure water analyzing apparatus (25) so that when the amount of impurities contained in the ultra-pure water thus produced exceeds a predetermined value, the produced ultra-pure water is returned to a suitable part in said ultra-pure water production apparatus, depending on the amount of impurities thus detected, starting from which ultra-pure water production is redone, and further a bypass containing a degassing device (28) is disposed on the piping for the ultra-pure water in the downstream of said ultra-pure water analyzing apparatus (25) so that when bubbles are detected by said analyzing apparatus, the ultra-pure water is degassed by said degassing device (28), flowing there-through.

28. An apparatus for analyzing impurities in liquid according to Claim 26, in which said light source (3) used for said apparatus for analyzing impurities is a

carbon dioxide gas laser device.

29. An apparatus for analyzing impurities in liquid according to Claim 25, in which the liquid to be analyzed is industrial waste water, samples of which are prepared, and the samples are made flow through the cells of said first to third analyzing sets one after another so that the impurities contained in the industrial waste water are analyzed.

FIG. 1

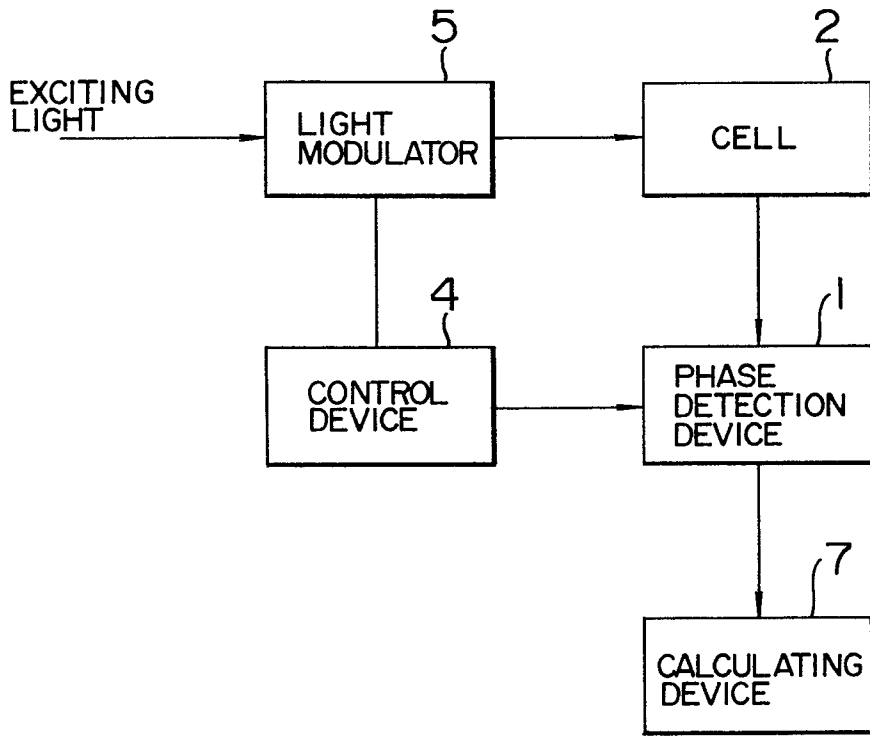


FIG. 2

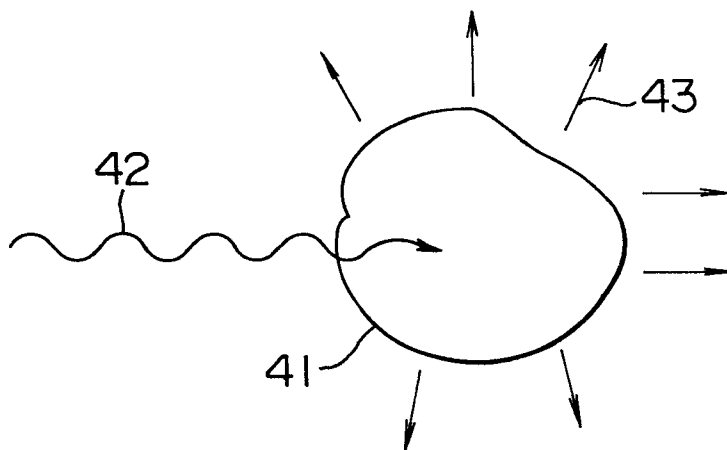


FIG. 3

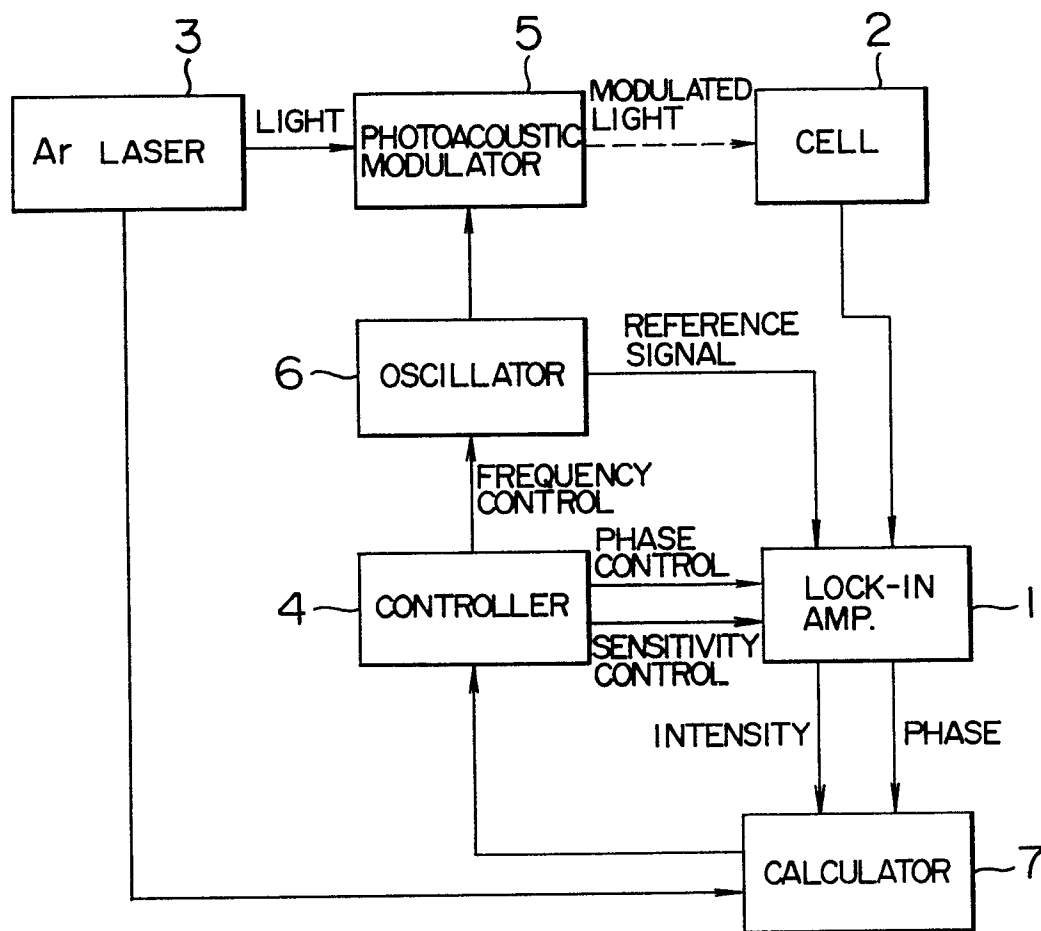


FIG. 4

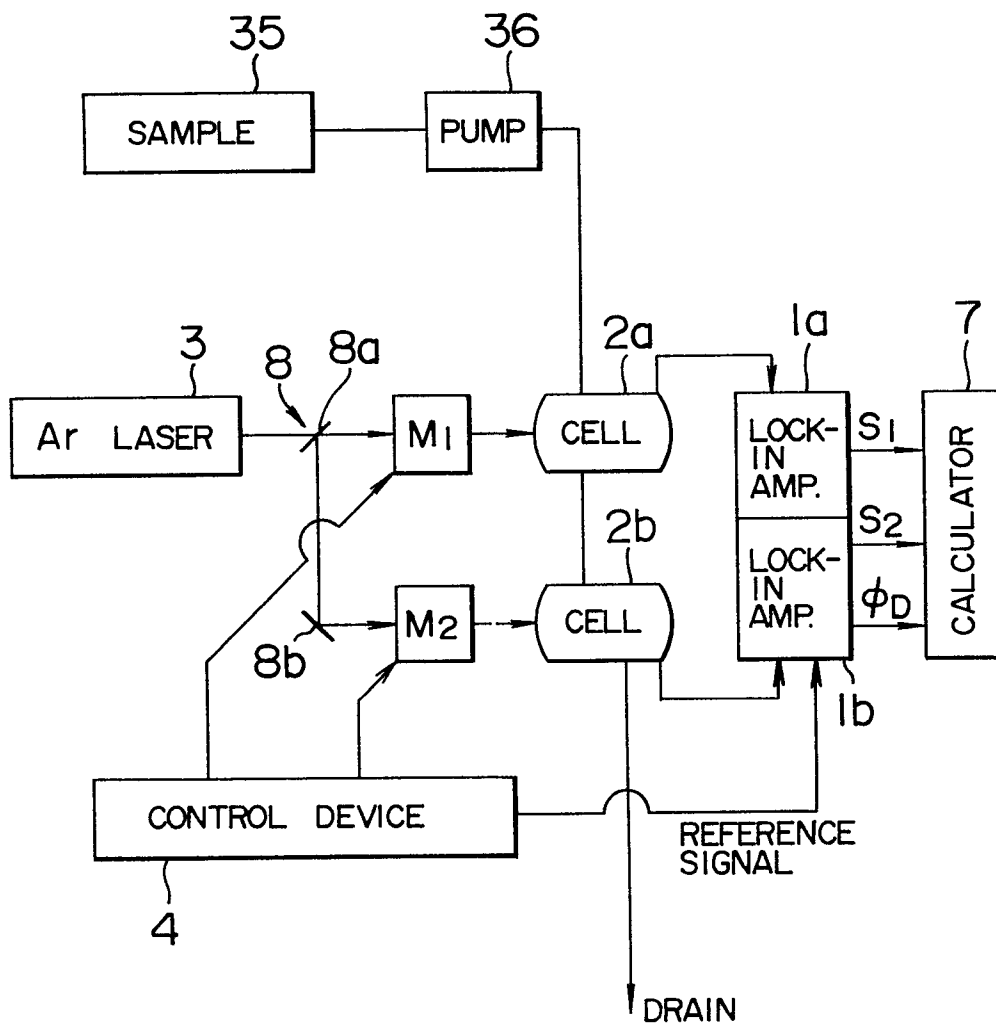


FIG. 5

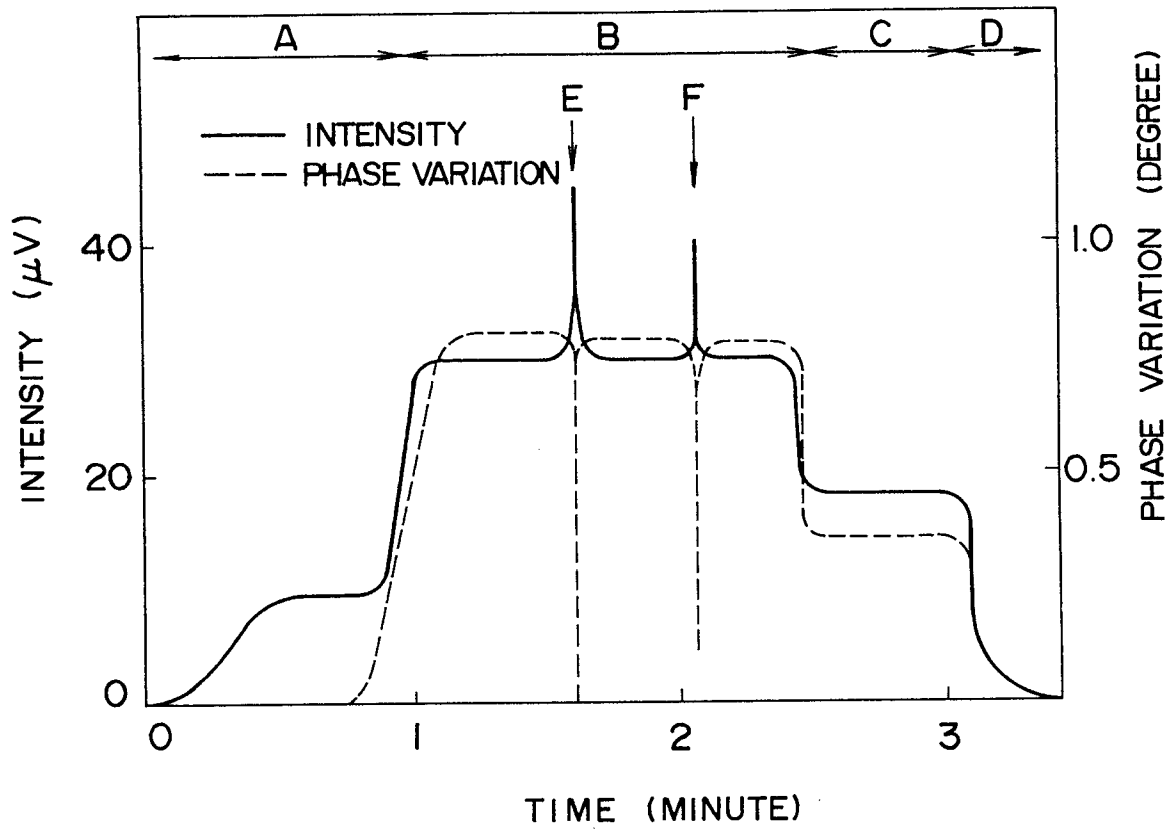


FIG. 6

